Localized versus extended systems in density-functional theory: some lessons from the Kohn-Sham exact exchange potential

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A long-standing puzzle in density-functional theory is the issue of the long-range behavior of the Kohn-Sham exchange-correlation potential at metal surfaces. As an important step towards its solution, it is proved here, through a rigorouos asymptotic analysis and accurate numerical solution of the Optimized-Effective-Potential integral equation, that the Kohn-Sham exact exchange potential decays as $\ln(z)/z$ far into the vacuum side of an *extended* semi-infinite jellium. In contrast to the situation in *localized* systems, like atoms, molecules, and slabs, this dominant contribution does not arise from the so-called Slater potential. This exact-exchange result provides a strong constraint on the suitability of approximate correlation-energy functionals.

Introduction In their seminal density-functional-theory (DFT) investigation of the electronic structure of metal surfaces, Lang and Kohn [1] pointed out that far outside the surface the Kohn-Sham (KS) exchange-correlation (xc) potential $V_{xc}(z)$ of DFT should behave like the classical image potential $- e^2/4z$, z being the distance from the surface. While from the physical view point this suggestion results attractive and reasonable, forty years later its rigorous proof is still an open question. Two kind of approaches are possible to address this difficult problem. One, followed already by some authors [2–4], is to consider exchange and correlation contributions to the KS xc potential *together*; we note, however, that as the correlation contribution should always be approximated, great care must be taken in approximating the corresponding exchange contribution in a *compatible* way. Within this context, it is not surprising that various asymptotics have been suggested for the KS exchange-only (x-only) potential along this pathway [2–4].

A second way to proceed, followed in the present Letter, is to exploit the fact that since the exchange-energy functional is known exactly, the corresponding KS exchange potential $V_x(z)$ can also be known exactly, by using the Optimized-Effective-Potential (OEP) method of DFT [5]. And knowing the exact $V_x(z)$, the analysis of the more elusive KS correlation potential $V_c(z)$ may be advanced on firmer grounds than previously. We have succeeded along this second type of approach, by proving rigorously that the asymptotic behavior of the KS exchange potential far into the vacuum side of a semi-infinite jellium is of the form $\ln(z)/z$. This analytical result is supported by a fully self-consistent numerical solution of the OEP integral equation, which describes accurately the KS exact exchange potential at the bulk, interface, and vacuum regions of our semi-infinite system.

Basic OEP equations for a metal surface The calculations presented below focus on the semi-infinite (SI) jellium model of a metal surface, where the discrete character of the positive ions inside the metal is replaced by a uniform distribution of positive charge (the jellium). The positive jellium density is given by $n_+(z) = \bar{n}\,\theta(-z)$, which describes a sharp jellium ($z < 0$) - vacuum ($z > 0$) interface at $z = 0$. The model is invariant under translations in the x, y plane (of normalization area A), so the single-particle KS orbitals of DFT can be rigorously factorized as $\varphi_{\mathbf{k}_\parallel, k}(\mathbf{r}) = e^{i\mathbf{k}_\parallel \cdot \boldsymbol{\rho}} \xi_k(z)/\sqrt{A\,L}$, where $\boldsymbol{\rho}$ and $\mathbf{k}_\parallel$ are the in-plane coordinate and wave vector, respectively. k and L refer to the remaining (continuous) quantum number and the normalization length, both along the z direction. The effective one-dimensional KS spin-degenerate orbitals $\xi_k(z)$ are the solutions of the KS differential equation (atomic units are used throughout)

$$\hat{h}_{\mathrm{KS}}^k(z)\xi_k(z) := \left[-\frac{1}{2}\frac{\partial^2}{\partial z^2} + V_{\mathrm{KS}}(z) - \varepsilon_k \right]\xi_k(z) = 0\ , \quad (1)$$

where ε_k are the KS eigenvalues, and $V_{\mathrm{KS}}(z) = V_{\mathrm{H}}(z) + V_{xc}(z)$. $V_{\mathrm{H}}(z)$ is the Hartree potential, and $V_{xc}(z) := \delta E_{xc}/\delta n(z)$, with $E_{xc} := E_{xc}[\{\varepsilon_k\}, \{\xi_k\}]$ and $V_{xc}(z)$ being the xc energy functional and potential, respectively, and $n(z)$ the ground-state electron density. The OEP integral equation whose solution provides the KS xc potential $V_{xc}(z)$ is compactly given as [6]

$$\int_0^{k_F} (k_F^2 - k^2)\Psi_k^*(z)\xi_k(z)\,dk\ +\ \mathrm{c.\ c.} = 0. \quad (2)$$

Here, $\Psi_k(z)$ are the so-called orbital shifts, defined by

$$\Psi_k(z) = \int_{-\infty}^{\infty} \xi_k(z') \Delta V_{xc}^k(z') G_k(z', z) \, dz' , \qquad (3)$$

with

$$G_k(z, z') = \frac{1}{\pi} P \int_0^{k_F} \frac{\xi_{k'}^*(z) \xi_{k'}(z')}{(\varepsilon_k - \varepsilon_{k'})} \, dk' \qquad (4)$$

being the KS Green function, $\Delta V_{xc}^k(z) = V_{xc}(z) - u_{xc}^k(z)$, and $u_{xc}^k(z) = [4\pi/A(k_F^2 - k^2)\xi_k^*(z)]\delta E_{xc}/\delta \xi_k(z)$; $u_{xc}^k(z)$ are usually referred to as orbital-dependent xc potentials. The symbol "P" in Eq. (4) denotes the "principal value", and k_F represents the magnitude of the Fermi wave vector [7]. The *exact* $V_{xc}(z)$ entering Eq. (2) is obtained as the solution of this integral equation, which must be solved self-consistently together with Eq. (1).

While for formal discussions the integral form of the OEP equation [Eq. (2)] is useful, it is often more convenient to recast it in the following fully equivalent form, after a well-established sequence of transformations [5, 6]:

$$V_{xc}(z) = V_{xc}^{\text{KLI}}(z) + V_{xc}^{\text{Shift}}(z) , \qquad (5)$$

where $V_{xc}^{\text{KLI}}(z)$ represents the so-called Krieger-Li-Iafrate (KLI) contribution [8, 9]:

$$V_{xc}^{\text{KLI}}(z) = \int_0^{k_F} \frac{|\xi_k(z)|^2}{2\pi^2 n(z)} \left[u_{xc}^{\,k}(z) + \overline{\Delta V}_{xc}^{\,k} \right] \widetilde{dk} , \qquad (6)$$

and

$$V_{xc}^{\text{Shift}}(z) = -\int_0^{k_F} \frac{\left[(k_F^2 - k^2)\Psi_k(z)\xi_k(z) + \Psi_k'(z)\xi_k'(z) \right]}{2\pi^2 n(z)} \widetilde{dk} , \qquad (7)$$

with $\widetilde{dk} = (k_F^2 - k^2) \, dk$, primes denoting derivatives with respect to the coordinate z and the ground-state electron density $n(z)$ being given by the following expression:

$$n(z) = \frac{1}{2\pi^2} \int_0^{k_F} (k_F^2 - k^2) |\xi_k(z)|^2 \, dk . \qquad (8)$$

Now we focus on the exchange contribution $V_x(z)$ to the KS xc potential of Eq. (5), as obtained by replacing the orbital-dependent xc potentials $u_{xc}^k(z)$ entering Eqs. (6) and (7) by their x-only counterparts $u_x^k(z)$ which are known exactly [10]. In this case, the first term on the rhs of Eq. (6) is easily recognized to be twice the position-dependent exchange energy per particle $\varepsilon_x(z)$, defined as the interaction between a given electron at z and its exact-exchange hole [10]. Noting that $2\varepsilon_x(z) = V_x^{\text{S}}(z)$, $V_x^{\text{S}}(z)$ being the so-called Slater potential [8], we write:

$$V_x(z) = V_x^{\text{S}}(z) + V_x^{\Delta}(z) + V_x^{\text{Shift}}(z) , \qquad (9)$$

where $V_x^{\Delta}(z)$ represents the contribution to the exchange potential $V_x(z)$ from the x-only counterpart of the second term on the rhs of Eq. (6).
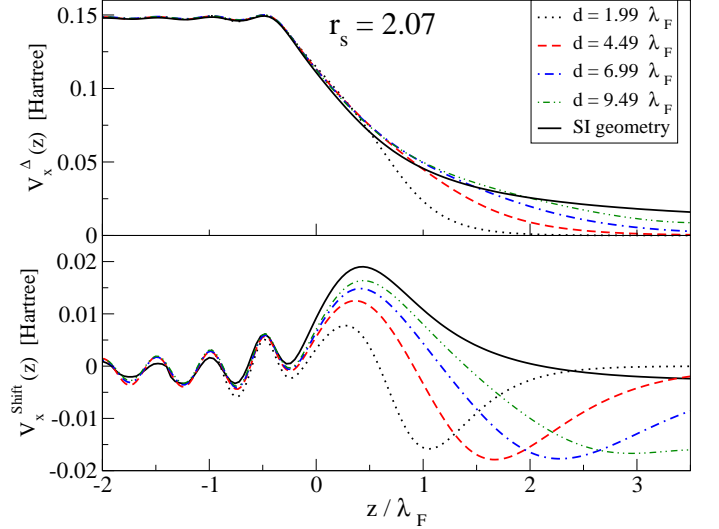

FIG. 1: (Color online) OEP self-consistent calculations of $V_x^{\Delta}(z)$ (top panel) and $V_x^{\text{Shift}}(z)$ (lower panel) for the SI geometry (solid line) and jellium slabs of various thicknesses d, for $r_s = 2.07$. $\lambda_F = 2\pi/k_F$ is the Fermi wavelength. The jellium-vacuum interface is at $z = 0$.

Numerical results In the case of the SI jellium, we have achieved the self-consistent numerical solution of the x-only counterparts of Eqs. (1) and (5). The KS equations have been solved by following the procedure explained in Ref. [10]; the orbital shifts were directly calculated from its definition in Eq. (3), with the KS Green function computed using the procedure of Ref. [11].

The correct asymptotics (at $z \to \infty$) of the Slater potential $V_x^{\text{S}}(z)$ have been reported for a SI jellium [12–14] and for jellium slabs [10], with the result that $V_x^{\text{S}}(z)$ decays in both cases as $-\beta/z$, but with a coefficient β that in the case of a SI jellium is electron-density dependent while for jellium slabs $\beta = 1$. Hence, here we focus on the remaining contributions: $V_x^{\Delta}(z)$ and $V_x^{\text{Shift}}(z)$.

OEP self-consistent calculations of $V_x^{\Delta}(z)$ and $V_x^{\text{Shift}}(z)$ for an electron-density parameter r_s corresponding to the average density of valence electrons in Al ($r_s = 2.07$) are plotted in Fig. 1, for the SI geometry and for jellium slabs of various thicknesses. We note that the bulk limit is correctly reproduced: $V_x^{\Delta}(z \to -\infty) = k_F/2\pi \simeq 0.148\,\text{Hartree}$ [15], while $V_x^{\text{Shift}}(z \to -\infty)$ presents small oscillations around zero, as it should be. In the case of jellium slabs, the numerical results were obtained using the procedure followed in Ref. [6].

In the vacuum, both $V_x^{\Delta}(z)$ and $V_x^{\text{Shift}}(z)$ decay exponentially for jellium slabs, as discussed before [6]. In the case of a SI jellium, however, the decay of $V_x^{\Delta}(z)$ and $V_x^{\text{Shift}}(z)$ turn out to be qualitatively different. This is seen in Fig. 2, where these quantities are plotted for $r_s = 6$, together with the Slater potential $V_x^{\text{S}}(z)$ and the
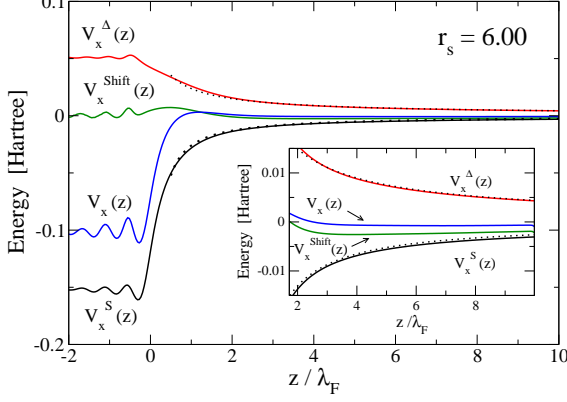
FIG. 2: (Color online) OEP self-consistent calculations of $V_x^S(z)$, $V_x^\Delta(z)$, and $V_x^{\text{Shift}}(z)$ for the SI geometry and $r_s = 6$. The jellium-vacuum interface is at $z = 0$. The bulk limits for $V_x^S(z)$, $V_x^\Delta(z)$, and $V_x(z)$ are correctly reproduced: $V_x^S(z \to -\infty) = -3k_F/2\pi \simeq -0.153$ Hartree [16], $V_x^\Delta(z \to -\infty) = k_F/2\pi \simeq 0.051$ Hartree, and $V_x(z \to -\infty) = -k_F/\pi \simeq -0.102$ Hartree. The analytical asymptotes of Eqs. (12) and (14) are shown by dotted lines. An enlarged view of the far-vacuum region is exhibited in the inset.

total $V_x(z)$. This figure shows that in the case of an extended SI jellium the asymptotics of $V_x(z)$ are dominated by $V_x^\Delta(z)$, which at large z is positive!

Analytical asymptotics In order to determine the actual asymptotic behavior of $V_x(z)$ in the vacuum region of a SI jellium, we first appeal to the asymptotic analysis of the KS orbitals $\xi_k(z)$ entering Eq. (1). One finds [13, 14]:

$$\xi_k(z \to \infty) \to \xi_{k_F}(z \to \infty)e^{-\alpha z \Delta k} \qquad (10)$$

and

$$n(z \to \infty) \to \frac{3\bar{n}}{4(\alpha k_F z)^2}\left|\xi_{k_F}(z \to \infty)\right|^2 , \qquad (11)$$

with $\alpha = k_F/\sqrt{2W}$, W being the work function, and $\Delta k = k_F - k$. This result is perfectly plausible: for $zk_F \gg 1$, the only k's that matter are those close to k_F and such that $z\Delta k \sim 1$, so the "window" for the relevant k's decreases linearly with distance. As for the electron density, it is interesting to note that it decays with an extra power z^2 in the denominator that is absent in the case of jellium slabs [10]; this is due to the fact that as $zk_F \gg 1$ the factor $(k_F^2 - k^2)$ in the integrand of Eq. (8) becomes effectively small, while in the case of jellium slabs this factor is always finite and the electron-density decay is purely exponential. This anticipates that qualitative differences might be expected between the asymptotics of localized (slabs) and extended (SI) systems.

By introducing Eqs. (10) and (11) into the expression for the Slater potential [the x-only counterpart of the

first term on the rhs of Eq. (6)], one finds the known result [10, 12–14]:

$$V_x^S(z \to \infty) = -\frac{(\pi + 2\alpha \ln \alpha)}{\pi(1 + \alpha^2)}\frac{1}{z} . \qquad (12)$$

Solamatin and Sahni (SS) [12] then derived the asymptotic structure of $V_x(z)$ from an approximate form of the so-called Sham-Schlüter integral equation relating $V_x(z)$ to the non-local Hartree-Fock self-energy and concluded that the asymptotics of $V_x(z)$ are embodied by half the Slater potential, i.e.: $V_x(z \to \infty) = \frac{1}{2}V_x^S(z \to \infty)$. SS supported their result by applying the definition of $V_x(z)$ as the functional derivative of the exchange energy (expressed in terms of the Slater potential):

$$V_x(\mathbf{r}) = \frac{1}{2}V_x^S(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}'\, n(\mathbf{r}')\frac{\delta V_x^S(\mathbf{r}')}{\delta n(\mathbf{r})}, \qquad (13)$$

and then suggesting that the contribution of the second term of Eq. (13) in the vacuum region is zero in the leading order of $1/z$. It is well known, however, that the second term of Eq. (13) contains another term of the form $\frac{1}{2}V_x^S(\mathbf{r})$ [15], leading, therefore, to an expression for $V_x(z)$ that contains the full Slater potential $V_x^S(z)$, and not one half of it, as noted by Nastos [13] and correctly given in Eq. (9) above. Moreover, here we prove that at large z the full $V_x(z)$ of Eq. (9) is not dominated by the Slater potential $V_x^S(z)$, but by $V_x^\Delta(z)$ instead.

Here we have succeeded, by introducing Eqs. (10) and (11) into the x-only counterpart of the second term on the rhs of Eq. (6), to obtain the following neat (positive!) expression for the leading contribution of $V_x^\Delta(z)$ to the long-range exchange potential:

$$\begin{aligned} V_x^\Delta(z \to \infty) &= \int_0^{k_F} \frac{\overline{\Delta V}_x^k}{2\pi^2 n(z \to \infty)}\left|\xi_k(z \to \infty)\right|^2 \widetilde{dk} \\ &= \frac{1}{2\pi\alpha z}\left[\ln(\alpha k_F z) + C\right] , \qquad (14) \end{aligned}$$

where $C \sim 0.96351$. In passing from the first to the second line we have replaced $\Delta V_x^k(z)$, which enters the calculation of $\overline{\Delta V}_x^k$, by its bulk value. That is, $\Delta V_x^k(z) \simeq \Delta V_x^k(z \to -\infty) = -k_F/\pi - u_x^k(z \to -\infty)$. The explicit (analytic) expression for $u_x^k(z \to -\infty)$ is obtained through a $\mathbf{k}_\parallel$ Fourier transform of the orbital-dependent exchange potential of a three-dimensional electron gas [16].

As for $V_x^{\text{Shift}}(z)$, we have first analyzed the asymptotics of Eq. (2) and then applied to it the operator $\hat{h}_{\text{KS}}^{k_F}(z)$. Solving the resulting equation for $V_x(z \to \infty)$, one recovers the asymptotic expressions for $V_x^S(z)$ and $V_x^\Delta(z)$ given by Eqs. (12) and (14), and one also obtains:

$$V_x^{\text{Shift}}(z \to \infty) = \frac{\alpha^2 z^2}{k_F \xi_{k_F}(z \to \infty)}\int_0^{k_F}\Delta k\, e^{-\alpha z \Delta k}$$

$$\times \left[\left(k_F - \frac{\alpha^2 \Delta k}{2}\right) + \alpha\frac{\partial}{\partial z}\right]\Psi_k(z \to \infty) \widetilde{dk} . \qquad (15)$$

At this point, we need $\Psi_k(z \to \infty)$, which we obtain from the asymptotics of the orbital-shifts differential equation $\hat{h}_{\text{KS}}^k(z)\Psi_k(z) = -\left[\Delta V_x^k(z) - \overline{\Delta V}_x^k\right]\xi_k(z)$. Noting that at $zk_F \gg 1$ *all* contributions in $\Delta V_x^k(z)$ tend to zero, the asymptotics of the orbital shifts are found to be given by the following expression:

$$\Psi_k(z \to \infty) \to [f(k) + zg(k)]\,\xi_k(z \to \infty)\,, \qquad (16)$$

where the first and second terms on the rhs are, respectively, the homogeneous and particular solutions of the orbital-shifts differential equation at $z \to \infty$. Here, $2g(k) = -\overline{\Delta V}_x^k/(\sqrt{2W} + \alpha\Delta k)$, and the explicit expression for $f(k)$ is not needed. After introduction of Eq. (16) into Eq. (15), we find that $V_x^{\text{Shift}}(z \to \infty)$ decays as $\ln(z)/z^2$. Hence, putting this together with Eqs. (12) and (14), we conclude that far outside a *semi-infinite* jellium the KS exact exchange potential decays as follows

$$V_x(z \to \infty) = \frac{\ln(\alpha k_F z)}{2\pi\alpha z}. \qquad (17)$$

Equation (17) represents the main result of this work. The asymptotics of Eqs. (12) and (14) are plotted in Fig. 2 (dotted lines), showing that they are in excellent quantitative agreement with our fully-self-consistent OEP numerical calculations at $z > \lambda_F$. In retrospective, the result of Eq. (17) looks natural for the SI case. For slabs, Eq. (9) yields $V_x(z \to \infty) = -1/z + \overline{\Delta V}_x^m$, m being the quantum number corresponding to the highest occupied slab level [6]; the first contribution is brought by the slab Slater potential $V_x^S(z)$, and the second contribution [brought by the slab $V_x^\Delta(z)$] is a constant which is chosen to be zero [5, 6]. In the SI case, however, while it is still true that the quantity $\overline{\Delta V}_x^{k_F}$ entering Eq. (14) is zero, the non-negligible contribution from $\overline{\Delta V}_x^k$ at $k_F - k < 1/z$ yields a $V_x^\Delta(z)$ potential that decays as $\ln(z)/z$ and dominates the asymptotics of the full $V_x(z)$.

Conclusions In summary, we have solved a long-standing problem relative to the long-range behavior of the KS exact exchange potential at metal surfaces, as an important step towards the understanding of the actual asymptotic behavior of the full KS *xc* potential. Through a rigurouos asymptotic analysis and accurate numerical solution of the OEP integral equation, we have shown that far into the vacuum side of a *semi-infinite jellium* the KS exact exchange potential decays as $\ln(z)/z$ (positive!). This analytical result, which does *not* arise from the Slater potential and is supported by a fully self-consistent numerical solution of the OEP integral equation, is in contrast to the situation in localized systems, like atoms, molecules, and slabs; as in the case of finite systems, for jellium slabs the asymptotics of the KS exchange potential arise from the full Slater potential, which decays as $-1/z$ [6]. Finally, we note that due to the fact that the full KS *xc* potential of a semi-infinite

metal should be expected to be absent of the dominant $\ln(z)/z$ exchange asymptotics, our exact-exchange result provides a strong constraint on the suitability of approximate correlation-energy functionals.

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